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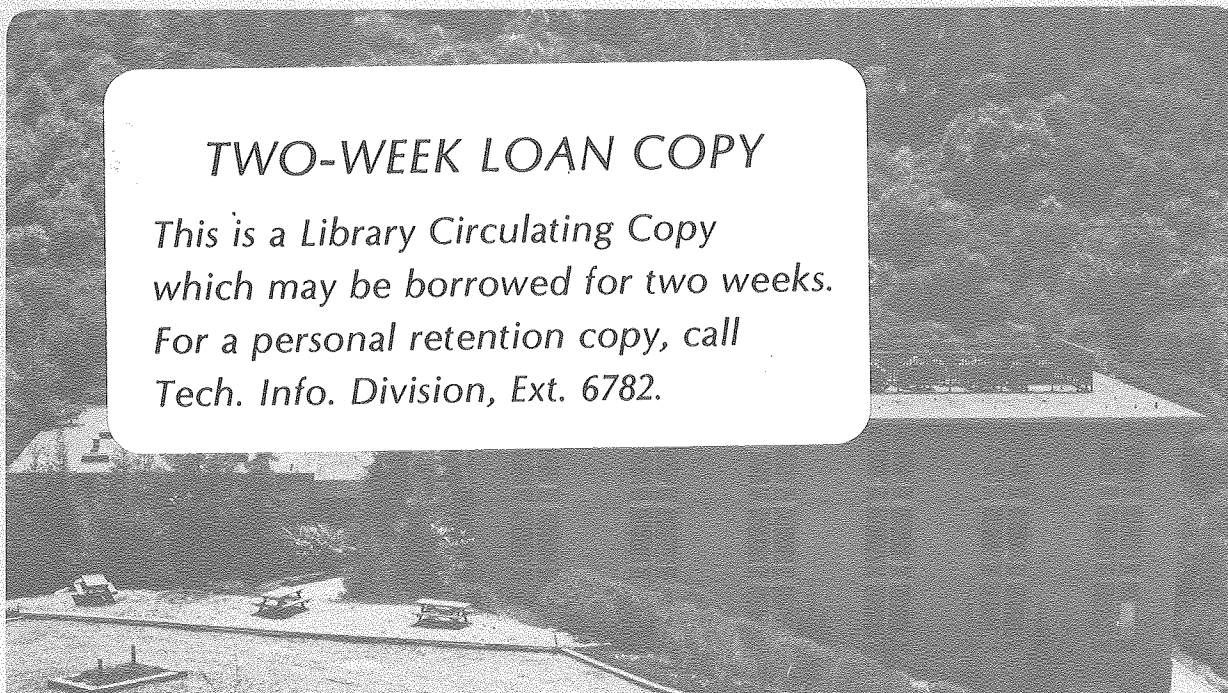
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PREPARATION AND STRUCTURAL CHARACTERIZATION OF α -NpF₅^{*}

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Introduction

Until recently, only the pentafluorides of uranium and protactinium had been prepared, although thermodynamic calculations suggested NpF₅ and possibly PuF₅ should be stable (1). Russian workers (2) have recently reported the synthesis of NpF₅ by the oxidation of NpF₄ in anhydrous hydrogen fluoride with KrF₂ at room temperature. Analysis of this material by spectroscopic and analytical methods showed it to be NpF₅. We have recently developed a new and relatively simple synthesis for UF₅ (3) by the reaction of UF₆ dissolved in anhydrous hydrogen fluoride with excess PF₃. A similar reaction has now been carried out with NpF₆ with the resultant product being α -NpF₅.

Experimental

NpF₆ was dissolved in anhydrous hydrogen fluoride at room temperature in a Kel-F tube. This solution was frozen at 77K and an excess amount of PF₃ was condensed onto the frozen solution. The liquid N₂ bath was removed and the solution was allowed to warm to room temperature. A bluish-white ppt formed during the warming process. After warming to room temperature the anhydrous hydrogen fluoride, PF₃ and PF₅, were removed by distillation. Samples for x-ray analysis were prepared in an argon atmosphere box.

X-ray powder patterns were obtained with a 114 mm Debye-Scherrer camera using copper K α radiation. All the lines in the powder pattern could be assigned on the basis of the α -UF₅ structure (4). The observed lines were fitted to the calculated pattern using the least squares program LCR-2 with the Nelson-Riley correction (5). The measured d-spacings, lattice parameters, and intensities are shown in Table 1.

TABLE 1
Powder Diffraction Data for α -NpF₅ at Room Temperature

Intensity ^a	hkl	Observed d spacings (Å)	Observed 2 θ ^b (deg)	Calculated 2 θ ^{b,c} (deg)
S+	110	4.611	19.25	19.26
S	101	3.678	24.20	24.23
M+	200	3.258	27.37	27.35
M+	211	2.440	36.83	36.84
M	220	2.308	39.03	39.04
W	002	2.222	40.60	40.54
S-	310	2.062	43.90	43.87
W+	112	2.004	45.24	45.24
M-	301	1.955	46.45	46.46
W+	202	1.840	49.55	49.58
W	321	1.676	54.77	54.74
W	400	1.633	56.35	56.38
W	222	1.604	57.47	57.53
W+	330	1.537	60.19	60.14
M-	312	1.514	61.22	61.24
M-	411	1.492	62.22	62.23
M-	420	1.459	63.77	63.77

^a S = strong, M = medium, W = weak.

^b Cu radiation - λ = 1.5418 Å.

^c Tetragonal lattice a = 6.53 \pm 0.03 Å, b = 4.45 \pm 0.03 Å.

Results

Although the reaction utilized for the synthesis of NpF_5 was a low temperature one, the structure of $\alpha\text{-NpF}_5$ determined is the same as $\alpha\text{-UF}_5$, the high temperature form. The $\alpha\text{-NpF}_5$ structure is consistent with the infrared and Raman spectra reported by the Russian workers (2).

The same reaction was run with PuF_6 but the product obtained was amorphous and had the same tan color as PuF_4 .

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